Monday Morning, November 4, 2002

Nanometer Structures
Room: C-207 - Session NS-MoM

Nanomechanics
Moderator: N.A. Burnham, Worcester Polytechnic Institute

9:00am **NS-MoM3 Structural Properties of Polymeric Nanostructures**, ***J.J. de Pablo***, University of Wisconsin-Madison **INVITED**

9:40am **NS-MoM5 Dynamics and Mechanics of Nanoscale Adhesive Contacts**, ***K.J. Wahl***, U.S. Naval Research Laboratory, *S.A.S. Asif*, Hysitron, Inc. **INVITED**

Recent advances in atomic force microscopy (AFM) and nanoindentation enable examination of surface mechanical properties of ultrathin films and compliant materials with far greater resolution and accuracy than ever before. In our laboratory, we have implemented dynamic mechanical analyses of nanoscale adhesive contacts using a 'hybrid' nanoindenter, coupling depth-sensing nanoindentation with AFM positioning capabilities. This combination allows surface sensitive, quantitative mechanical properties measurements of nanostructures and thin films, at a single point as well as while scanning. We illustrate these expanded capabilities with several examples: 1) a dynamic nanoscale Johnson-Kendall-Roberts (nano-JKR) adhesion test, and 2) scanning nanomechanics. The nano-JKR test allows study of processes that occur during the formation and breaking of adhesive contacts with diameters smaller than the optical limit, and can be used to measure dynamic visco-elastic properties including loss and storage moduli, adhesion energy, and strain energy release rate. Scanning nanomechanics provides a means of directly imaging mechanical response and properties with sub-micron spatial resolution. We will discuss how these new capabilities can be used to test the models and limits of continuum contact mechanics.

10:20am **NS-MoM7 Creep Compliance and Stress Intensity in Small Viscoelastic Contacts**, ***W.N. Unertl***, University of Maine, *M. Giri*, Hewlett-Packard - Corvallis

Adhesive contacts to viscoelastic materials with dimensions smaller than a few microns are difficult to analyze. This is due, in part, to the inability to measure the contact size directly. One consequence is the lack of a quantitative method to measure time-dependent mechanical properties. We demonstrate a method to overcome these difficulties. First, we extend a theory of viscoelastic contact[1] to show how the contact radius, the stress intensity at the contact edge, and the creep compliance function can be extracted directly from load vs. deformation data. Then, we apply this analysis to load controlled indentation data for a paraboloidal diamond probe on a styrene-butyl acrylate substrate with 27 C glass transition temperature. The probe is brought into contact, the load is increased linearly to a predetermined maximum, and then decreased until the contact ruptures. Loads up to 3 mN result in deformations up to 2 mm in depth depending on the loading rate and contact time. Viscoelastic effects, indicated by the occurrence of maximum penetration after maximum load, were largest for contact times near 20 s. Calculated contact radii are up to 6 mm. The creep compliance for this material is described by a power law in time with exponent near 0.8. In contrast to predictions of simple fracture mechanics models, the stress intensity is not a unique function of the speed of the contact edge. This suggests either an interaction potential between the probe and polymer that is rate dependent or a polymer response that is non-linear under the conditions that occur at the contact periphery in these experiments. These results bring into question all previously reported nanoscale measurements of the mechanical properties of viscoelastic materials.

[1]C.Y Hui, J.M. Baney, and E.J. Kramer, Langmuir 14, 6570 (1998).

10:40am **NS-MoM8 Mechanical and Electrical Properties of $Mo_3Se_3^-$ Nanowires and Nanowire-networks**, ***A. Heidelberg***, *G. Staikov, J.W. Schultze,* Heinrich-Heine-Universität Düsseldorf, Germany, *J.J. Boland*, University of North Carolina at Chapel Hill

Nanowires and nanotubes have attracted enormous interest as potential building blocks for nanotechnology.[1] This interest can be traced to the novel structural, mechanical and electronic properties of these nanomaterials. Here we describe a study that measures these properties in the case of the $(Mo_3Se_3)^-$-nanowire system.[2] The mechanical properties of single nanowires or bundles were studied using an SPM-nanomanipulator. This instrument allows us to controllably apply forces (μN-nN range) to supported Mo_3Se_3-nanowires to effect nanoscale manipulations. Using the lateral force data of the manipulations, the mechanical properties like Youngs modulus and tensile strength of the nanowires can be calculated. The electrical properties of bare $LiMo_3Se_3$-nanowires have previously been shown to have metallic behaviour.[3] Exchanging the Li-counterion to alkylammonium, alkylpyridinium or alkylpiperazinium counterions produces network structures of the nanowires with a defined interwire spacing. Conductivity measurements at different temperature and oxidation times show that these networks act as percolation networks and have semiconducting behaviour. In addition the corrosion rate of the Mo_3Se_3-nanowires is slowed down in the wire networks, demonstrating that the organic coating forms partially insulating layers.

[1] J. Hu, T. W. Odom, C. M. Lieber; Acc. Chem. Res. 32 (1999) 435
[2] J. M. Tarascon, F. J. DiSalvo, Solid State Commun. 52 (1984) 227
[3] J. H. Golden, F. J. DiSalvo, J. M. J. Fréchet, Chem. Mater. 7 (1995) 232.

11:00am **NS-MoM9 Towards the Sensing of Atomic Interactions by Nanoindentation with Extremely Sharp Tips**, ***J. Fraxedas***, ICMAB-CSIC, Spain, *S. Garcia-Manyes*, CBEN and University of Barcelona, Spain, *P. Gorostiza*, University of California, Berkeley, *F. Sanz*, CBEN and University of Barcelona, Spain

A force F applied to a surface acts directly on the surface atoms and is transmitted to the bulk atoms via the crystal lattice. The bonds play thus a crucial role in the mechanical response because of their strength and spatial distribution. For a point force only few atoms are involved. In this case the elastic deformation of the surface critically depends on in-plane interactions. In order to demonstrate the relevance of such interactions we have done nanoindentation experiments on 2D materials and ionic single crystals with an AFM. The stiffness k of the crystal and an estimated radius d_s of the elastically perturbed surface can be evaluated from expression $F(\delta)=k\,\delta(1-d_s/\sqrt{(\delta^2+d_s^2)})$,[1] where δ stands for the surface deformation. k is related to the Debye frequency ω_D ($k_D=m\omega_D^2$), where m represents the mean atomic mass. The calculated values of k_D are very close to the experimentally derived values of k (i. e., k=84±13 Nm^{-1} and k_D=86 Nm^{-1} for NaCl). Nanoindentation thus reveals the collective behavior of nanoscale volumes since many atoms are involved in the process (ca. 140 ion pairs for the alkali halides). We observe that $k/d_s=c_{11}$, where c_{11} represents the (1,1) component of the elastic tensor. Feynman developed a simple model relating the anion-cation interatomic interaction k_{ac} to elastic constants for small strains for NaCl-type crystals assuming central forces.[2] Within this approximation we obtain $k_{ac}<13$ Nm^{-1}, in good agreement with k_{ac}=10-12 Nm^{-1}, obtained in the harmonic limit from long wavelength TO phonon frequencies.

[1] J. Fraxedas, S. Garcia-Manyes, P. Gorostiza, F. Sanz, Proc. Natl. Acad. Sci. USA 99, 5228 (2002)
[2] R. P. Feynman, R. B. Leighton, M. Sands in The Feynman Lectures on Physics (Addison-Wesley, 1964), pp. 10.

11:20am **NS-MoM10 Playing Nano-squeeze with Fluids**, ***M. Heuberger***, ETH Zuerich, Switzerland **INVITED**

It was found, over two decades ago, that some fluids exhibit a remarkable spectrum of new properties when confined between two atomically smooth and nearly parallel mica sheets in the surface forces apparatus. Oscillatory or structural forces, as well as a dynamic solidification of such thin fluid films were reported. What do these fluids have in common and what can we learn from their behavior? Well-established thermodynamic measurements of fluids adsorbed into porous materials suggest a shift of critical points, transition temperatures and enthalpies, which are more pronounced the smaller the pore radius. Recently, unexpected density and film-thickness fluctuations were discovered in these confined fluid films. Can a shift of thermodynamic quantities in small volumes account for the observed fluctuations? Recent results reveal a relationship between the thickness of the mica sheets and the amplitude of the fluctuations in the eSFA. I will present new details of the contact mechanics at sub-Angstrom resolution and discuss the role of nano-particles in SFA measurements. A comparison of measurements obtained with conventionally prepared and particle-free surfaces is shown. A mechanical model involving nano-particles is invoked to explain the observed effects.

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